

Magnetic Properties of $\text{Mg}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ Nanoferrites

J.Z. Msomi · T. Moyo · H.M.I. Abdallah

Received: 7 July 2011 / Accepted: 11 July 2011 / Published online: 9 August 2011
© Springer Science+Business Media, LLC 2011

Abstract We report the magnetic properties of $\text{Mg}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1.0$) nanosize compounds with particle sizes between 8 nm and 15 nm. The evolutions of the properties as a function of composition have been investigated by X-ray diffraction, Mössbauer, and SQUID magnetometry. Pure cubic spinel could be obtained under a low reaction temperature of 200°C in all the samples. Impurity phases have been observed in compounds annealed at above 900°C. Magnetic relaxation is observed in samples with particles of about 8 nm. The spectra with particle sizes larger than 10 nm could be fitted with at least two sextets attributed to Fe^{3+} ions on tetrahedral (A) and octahedral (B) sites. The magnetization measurement indicates superparamagnetic behavior in nanosized compounds.

Keywords Glycolthermal · Ferrite · Nanoparticles · Magnetic property

1 Introduction

The Mg–Mn ferrites are appropriate for memory and switching circuits in digital computers due to their rectangular hysteresis characteristics. They are also suitable for phase shifters because of their high squareness and low coercive

fields [1, 2]. Mn doped Mg ferrites are also used in high frequency applications because of their high initial permeability and low values of relative loss factor [3]. Superparamagnetic nanoparticles are relevant in modern technologies such as magnetic resonance imaging contrast agents, ferrofluids, and magnetocatalytic refrigeration [4]. The superparamagnetic properties of ferrite materials can be controlled by particle sizes and concentration of nonmagnetic atoms. Efforts are being made to produce fine particles and to find dopants that can improve the properties and find new applications. Of interest are the properties of Mg–Mn substituted ferrites. In this work, we have produced $\text{Mg}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1.0$) fine particles and investigated their magnetic properties.

2 Experimental Details

High purity nitrates were used as starting materials to make 0.1 M solutions for the glycolthermal process. 5 M solution of excess KOH was then slowly added to the mixture of nitrate solutions under rapid stirring until full precipitation was achieved. The precipitate was washed several times by deionized water and finally by 200 ml of ethanol. The clean precipitate was dispersed in 300 ml of ethylene glycol under rapid stirring. The mixture was then placed in a 600 ml stainless steel pressure vessel (Watlow series model PARR 4843 reactor). The pressure vessel was heated to 200°C and the gauge pressure was allowed to gradually rise to 100 psi. These conditions were held for 6 hours. The cooled products after boiling were filtered and washed by deionized water and ethanol. The recovered synthesized powders were dried under a 250 W infrared lamp, homogenized, and divided into several specimens, which were sintered at different temperatures until single phase cubic spinel structure was formed.

J.Z. Msomi (✉)
Department of Physics, University of the Free State,
Private Bag X13, Phuthaditjhaba 9866, South Africa
e-mail: msomijz@qwa.uovs.ac.za

T. Moyo · H.M.I. Abdallah
School of Physics, University of KwaZulu-Natal,
Private Bag X54001, Durban 4000, South Africa

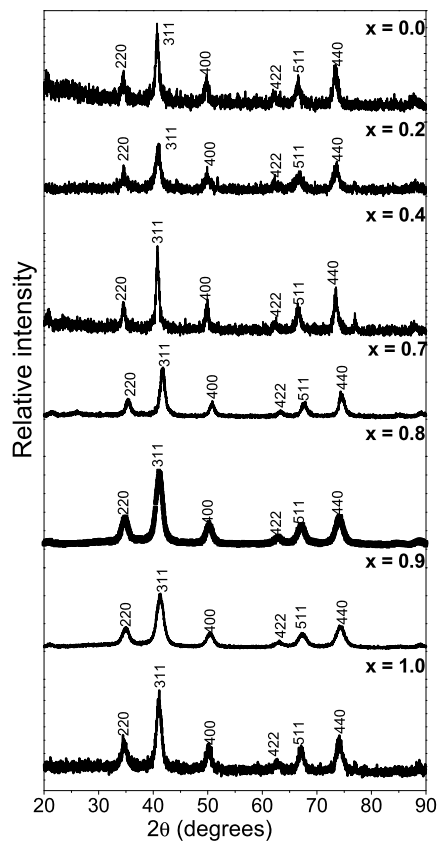


Fig. 1 XRD spectra for $\text{Mg}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$

The X-ray diffraction (XRD) patterns of the samples were obtained using a monochromatic beam of $\text{CoK}\alpha$ radiation ($\lambda = 1.7903 \text{ \AA}$) on a Phillips diffractometer (type: PW1710). The Mössbauer spectra were recorded at about 300 K using a conventional constant acceleration Mössbauer spectrometer with a ^{57}Co source sealed in a Rh matrix. The standard iron foil was used to calibrate the Mössbauer spectra. Variations of the magnetization as a function of applied magnetic field (up to 5 T) and temperature (2–380 K) have been studied using a SQUID MPMS produced by Quantum Design.

3 Results and Discussions

Figure 1 shows the XRD spectra for the as prepared $\text{Mg}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($0 \leq x \leq 1.0$) nanosized samples. All the major peaks are characteristic of a pure cubic spinel structure. No impurity phases have been detected in all the as prepared samples.

The broader peaks indicate smaller particles. The grain sizes shown in Table 1 were estimated from the most intense 311 XRD peak using the Debye–Scherer equation [5]. The particle size ranges between 8 nm and 15 nm. The typical variations of XRD patterns with an annealing temperature

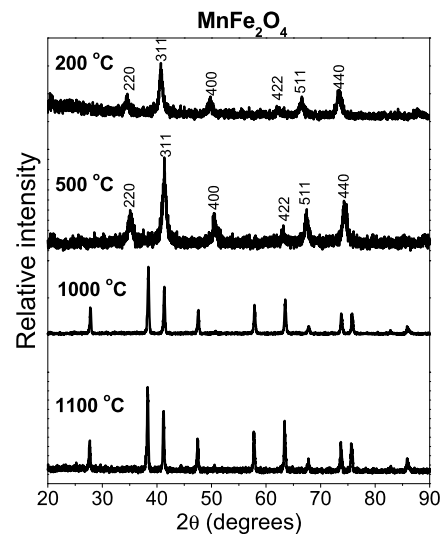


Fig. 2 Variation of XRD spectra for $\text{Mg}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0$)

is shown in Fig. 2 for $x = 0$ (MnFe_2O_4). The single phase cubic spinel structure was destroyed after annealing the as prepared samples at temperatures higher than 900°C . The impurity phase may be due to Fe_2O_3 and Mn_2O_3 phases. The spinel crystal structures formed appear to be unstable at high temperatures.

The typical Mössbauer spectra of the as prepared and annealed samples are shown in Figs. 3(a) and 3(b), respectively. The lines in spectra for samples with grains smaller than 9 nm are broadened. The well-resolved six line Mössbauer spectra are observed only for samples with particles larger than 9 nm. The spectra for samples with larger grains (at least about 10 nm) could be fitted with three sextets and one doublet. Each sextet corresponds to Fe^{3+} ions in an ordered spin state distributed on tetrahedral (A) or octahedral (B) sites. The third sextet with low hyperfine field may be associated with Fe^{3+} ions in grain boundaries [6]. A doublet is associated with particles in a paramagnetic state. Sextets and doublets were assigned to A or B sites based on the fitted results of isomer shifts and hyperfine fields. The A site isomer shift and hyperfine fields are supposed to be lower at the A site because of higher symmetry. The fitted data of isomer shifts, hyperfine fields, and line widths are shown in Table 1. There is no significant change in isomer shifts with composition. This indicates that the s electron charge distribution of Fe^{3+} ions is not significantly affected by Mg concentration. This is expected as Mg ions are replacing Mn ions in $\text{Mg}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ oxides. The concentration of Fe ions is not affected by Mg substitution. The hyperfine fields of compounds annealed at 700°C (bracketed values) are also shown in Table 1. A general increase in hyperfine fields with increasing grain size is observed. The reduced values of hyperfine fields for samples with smaller grains can be

Fig. 3 Variation of Mössbauer spectra for (a) as prepared and (b) annealed (700°C) $Mg_xMn_{1-x}Fe_2O_4$ oxides with x

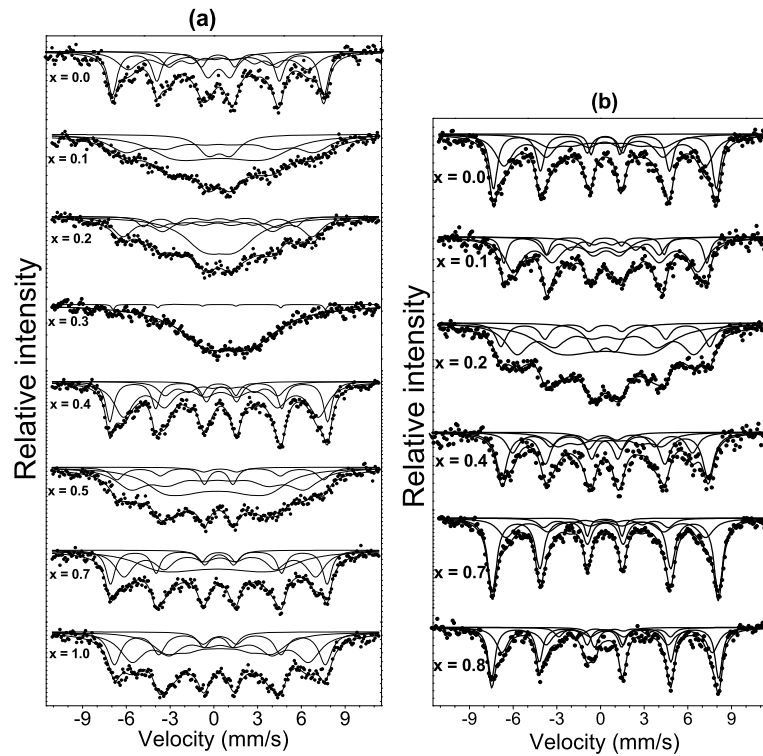


Table 1 Variation of grain size (D), isomer shifts (IS), hyperfine fields (H) and line width (L) on A and B sites with x (The bracketed values are for samples annealed at 700°C (a))

T_A (°C)	D (nm) ± 0.2	IS_A (mm/s) ± 0.03	IS_B (mm/s) ± 0.04	H_A (kOe) ± 3	H_B (kOe) ± 2	H_{3rd} (kOe) ± 0.02	L_A (mm/s) ± 0.01	L_B (%) ± 0.03
0	14.8	0.31	0.30	401 (429)	469 (475)	239 (243)	0.86	0.40
0.1	13.7	0.36	0.33	393	432	240	0.76	0.27
0.2	11.9	0.25	0.38	402 (445)	324 (378)	252 (213)	0.82	0.48
0.3	8.4	(0.15)	(0.33)	(399)	(459)	(232)	(0.51)	(0.48)
0.4	16.3	0.34	0.48	415	463	240	0.80	0.34
0.5	8.8	0.25	0.44	368	440	224	1.27	0.53
0.7	10.0	0.41	0.34	408 (426)	461 (482)	257 (266)	0.76	0.37
0.8	8.8	(0.46)	(0.32)	(448)	(483)	(238)	(0.51)	(0.29)
1.0	9.2	0.44	0.41	375	448	227	0.98	0.52

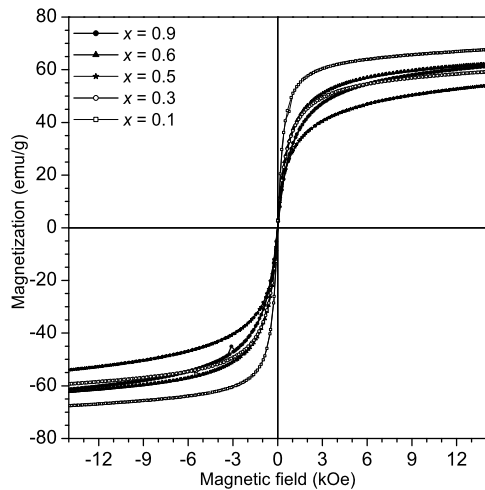


Fig. 4 Typical hysteresis curves for $Mg_xMn_{1-x}Fe_2O_4$

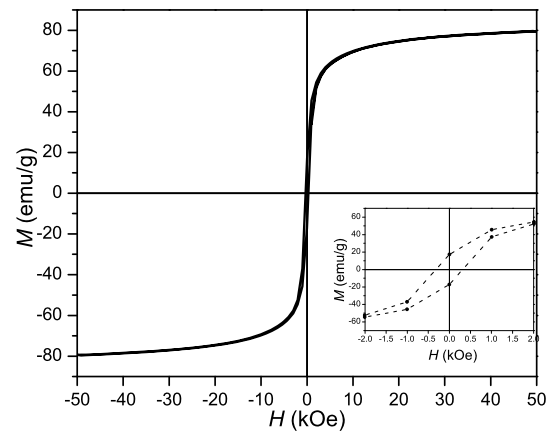
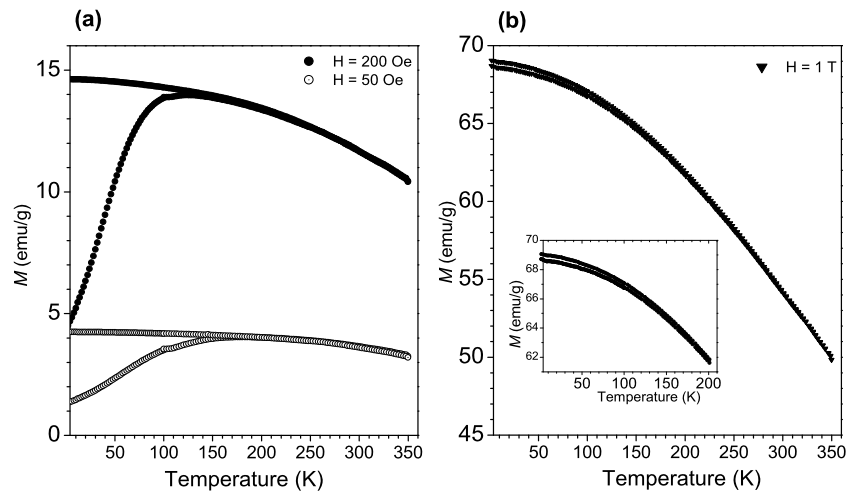


Fig. 5 Typical hysteresis curves for $Mg_xMn_{1-x}Fe_2O_4$ ($x = 0.5$) measured at 4 K.

Fig. 6 Variation of FC and ZFC magnetization as a function of temperature measured in a magnetic field of (a) 100 Oe and 200 Oe and (b) 1 T for $\text{Mg}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5$)



attributed to collective excitations in small particles as explained in [7].

The typical variations of magnetization as function of magnetic field are shown in Fig. 4. The “S” like shape of the magnetization curves with zero coercive fields indicate superparamagnetic behavior of the fine particles.

This relates well with a doublet associated with the paramagnetic nature of particles required to get good fits to the Mössbauer data. Figure 5 shows typical magnetization curve measured at 4 K in an applied field up to 5 T. No saturation is observed even in a field of 5 T. The insert in Fig. 5 is the amplified view of magnetization against applied low fields. The coercive fields increase at low temperature as expected.

Figures 6(a) and 6(b) show the typical variation of magnetization as a function of temperature for $x = 0.5$. During field cooling (FC), the oxides were cooled from 350 K to 2 K in the presence of an external magnetic field of 100 Oe, 200 Oe, and 1 T. The lower curve is obtained for ZFC and the upper curve is for the FC. The magnetization in the FC curve decreases continuously with increasing temperature. The width of the peak in ZFC curve is associated with particle size distribution. A particle with a particular size has a certain blocking temperature. A wide peak observed in our samples indicates wide distribution of particle sizes. The FC magnetization tends to saturate at about 2 K. The insert in Fig. 5(b) shows an amplified view of magnetization measured at low temperatures. The bifurcation temperature is about 200 K.

4 Conclusions

The $\text{Mg}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ compounds with particle size between 8 nm and 15 nm have been produced. The crystal structure appears to be unstable at sintering temperatures above 900°C. The magnetization curves with zero coercive field indicate superparamagnetic behavior of the particles.

Acknowledgements One of the authors (J.Z.) wishes to thank the NRF REDIBA programme for financial support and the Institute of Inorganic Chemistry (Czech Republic) for magnetization measurements.

References

1. Singh, M.: *J. Magn. Magn. Mater.* **299**, 397 (2006)
2. Lakshman, A., Rao, P., Rao, K.: *J. Magn. Magn. Mater.* **284**, 352 (2004)
3. Kumar, G., Chand, J., Verma, S., Singh, M.: *J. Phys. D, Appl. Phys.* **42**, 155001 (2009)
4. Chen, Q., Rondinone, A.J., Chakoumakos, B.C., Zhang, Z.J.: *J. Magn. Magn. Mater.* **194**, 1 (1999)
5. Ashiq, M.N., Saleem, S., Malana, M.A., Anis-Ur-Rehman, J.: *J. Alloys Compd.* **486**, 640 (2009)
6. Chinnasamy, C.N., Narayanasamy, A., Ponpandian, N.: Chatopdhyay Shinoda, K., Jeyadevan, B., Tohji, K., Nakatsuka, K., Furubayashi, T., Nakatani, I.: *Phys. Rev. B* **63**, 184108 (2001)
7. Mørup, S.S.: *Hyperfine Interact.* **60**, 959 (1990)